SCAVENGING RATIOS OF ACIDIC POLLUTANTS AND THEIR USE IN LONG-RANGE TRANSPORT MODELS

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Your paper "Scavenging ratios of acidic pollutants and their use in long-range transport models"

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Abstract

The scavenging ratios for SO_2, SO_4^{2-}, and NO_3^- vary markedly (over two orders of magnitude) between precipitation events and are shown to possess log-normal distributions. Using a constant value of scavenging ratio as an input parameter into a model, as is generally practiced, will lead to significant errors in model calculations.

Scavenging ratios for SO_4^{2-} show little spatial variation. The spatial variability for NO_3^- is larger. Also, the scavenging ratios for NO_3^- suggest that in cloud formation of NO_3 may be important.

1. Introduction

Current long range transport models employing a linear wet and dry scavenging scheme assume that wet deposition of pollutants is given by the product of a scavenging coefficient Λ (s^{-1}) and the integral over the mixed layer depth (h) of the pollutant concentration in the air. If one defines scavenging ratio W as the ratio of pollutant concentration in precipitation to its air concentration, then W equals $\frac{\Lambda h}{p}$ where p is the precipitation rate. This assumes that the pollutant is uniformly distributed in the mixed layer.

Authors differ in their choices of scavenging parameters. Elliassen (1978) assumes Λ to be constant, Shannon (1980) defines Λ as a power law function of p , Ellenton et al. (1983) assume W to be constant. Unless Λ(or W) is derived from fundamental principles of in-cloud chemical transformation and mass transfer of pollutants to water droplets in the clouds, and the functional dependence on dominant variables is expressed explicity, one has no guidance on evaluating them by the precipitation events. On the other hand, physical and chemical processes in the atmosphere dictate that Λ or W should vary markedly between precipitation events.

Since a linear treatment of the scavenging processes leads to an exponential decay type solutions to the pollutant species, the variability of Λ(or W) cannot be simply approximated by using an average value for long term simulations as is generally practised by the modellers. It is shown in Section 3 of this paper that ignoring the variability of Λ(or W) may lead to serious errors in the final model computations.

The purpose of this paper is to present the distribution of W for SO_2, SO_4^{2-} and NO_3^- as derived from data from a monitoring network (APIOS - Acidic Precipitaiton in Ontario Study) in Ontario, Canada and to show the implications of this variability of W on model calculations. It is shown that W possesses a log-normal distribution. Using an average value of W in Lagrangian long-range transport models leads to an under-prediction of concentration and deposition of sulphur in remote areas.

2. Network Description

As part of the APIOS, Ontario operates two networks monitoring both wet and dry deposition. One network samples on a daily basis (Chan et al. 1982) and the other one 28-day basis (Chan et al. 1984). This paper presents data obtained in the former network.

The daily network has been in operation since July, 1980 at one site (Dorset) in central Ontario. It was expanded to 16 sites in 1981 which are clusterd into 4 groups with spatial separation of more than 1,000 km. Wet deposition is collected at all 16 sites with Aerochem Metrics wet-only samplers at all times except during the winters of 1980/81 and 1981/82 when 24 hour bulk samplers were used. Dry deposition is estimated by measuring ambient air concentrations using a lo-vol filtration technique at 1 station of each of the 4 clusters. Samples collected on the teflon prefilters are analyzed for particulate SO_4^{2-}, NO_3^- and NH_4^+ whereas those on the downstream nylon and impregnated K_2CO_3-glycerol Whatman 41 filters are analyzed for gaseous HNO_3 and SO_2 respectively. Both daily wet and dry samples are collected typically around 8 a.m. Data presented here are obtained from Charleston Lake (44°29'54"N, 76°02'30"W), Dorset (45°13'23"N, 78°55'49"W), Longwoods (42°53'02"N, 81°28'50"W) and

Fernberg (47°56'51"N and 91°29'26"W). The 3 former sites are located in Ontario. The last site is located in Minnesota where the Ontario instruments are co-located with those operated by the United States Environmental Protection Agency at Duluth.

3. Results and Discussion

Only stations with both precipitation (mg l^{-1}) and air (ug m^{-3}) concentration results are examined for scavenging characteristics of the S and N compounds in 6 different combinations:

$$W_1 = \frac{S\text{-}SO_4^{2-}\ (\text{precip.})}{S\text{-}SO_4^{2-}\ (\text{air})}$$

$$W_2 = \frac{S - SO_4^{2-}\ (\text{precip.})}{S - SO_2\ (\text{air})}$$

$$W_3 = \frac{S - SO_4^{2-}\ (\text{precip.})}{S - SO_4^{2-}\ (\text{air}) + S - SO_2\ (\text{air})}$$

$$W_4 = \frac{N - NO_3^-\ (\text{precip.})}{N - NO_3^-\ (\text{air})}$$

$$W_5 = \frac{N - NO_3^-\ (\text{precip.})}{N - HNO_3\ (\text{air})}$$

$$W_6 = \frac{N - NO_3^-\ (\text{precip.})}{N - NO_3^-\ (\text{air}) + N - HNO_3\ (\text{air})}$$

The above combinations are necessary as SO_4^{2-} and NO_3^- in precipitation do not originate entirely from particulate SO_4^{2-} and NO_3^- in air. Some unknown portions originate also from SO_2 and HNO_3 (and possibly NO_x). W_1, W_2, W_4 and W_5 yield upper bounds of scavenging ratios for SO_4^{2-}, SO_2, NO_3^- and HNO_3. In order to account for the fraction of precipitation concentration due to other co-existing species in the air, W should be scaled accordingly. In the case of $SO_4^=$ and SO_2 in air, Henry's law calculations could be applied (Barrie, 1981). It is recommended that factors 0.9 and 0.1 should be applied to W_1 and W_2 as a first order approximation as it has been found that SO_2 correction is less than 10% (Barrie, 1983). The correction for the N species is not well understood, however, Huebert et al. (1983) have reported a ratio of W_4 to W_5 being five by snow scavenging.

The calculated ratios are tested for normal and log-normal distributions using Kolmogorov-Smirnov statistics (Pollard, 1977), when the number of data points is greater than 50 (otherwise the Shapiro-Wilk statistics is used). Basically, this test compares the largest absolute cumulative difference between the tested sample distribution and the normal distribution with the Kolmogorov-Smirnov statistics (or Shapiro-Wilk (w) statistics) of the same sample size. When the test value (D_{stat}) is greater than the critical value ($D_{0.05}$) at 5% significance level, it indicates that the sample possibly does not come from a normal distribution. In other words, we may conclude that the sample distribution is not normal with a 5% chance of making a wrong conclusion. However, only when the test value (D_{stat}) is well below the critical value ($D_{0.05}$), we may have high confidence in concluding that the sample distribution is normal. Results of the test (Tables 1 to 6) indicate that the observed scavenging ratios follow a log normal distribution well. The following points are noteworthy.

a. There is little spatial variability in SO_4^{2-} scavenging ratio.

b. The spatial variation in NO_3^- scavenging ratio is larger reflecting non-uniform change in concentration of NO_3^- in precipitation and NO_3^- and HNO_3^- in air geographically.

c. Using Junge's scheme (1963) of rainout efficiency ϵ_i, or $W_i \times 10^{-6}$ iin our notation) Hidy (1982) indicated that rainout efficiency could be identified with the scavenging ratio based on ground level precipitation and air measurements. With simplifying assumptions including (i) below cloud scavenging is small compared with in-cloud scavenging processes; (ii) clouds have an average 1 g m^{-3} liquid-water content; (iii) precipitation composition is identified with cloud water composition and can be related to ambient air concentration which is taken to be constant with height, ϵ_i is expected to fall in the range of zero to unity. The fact that W_6 ($\times 10^{-6}$) is greater than unity most of the time suggests that NO_3^- in precipitation cannot be simply explained by its air concentration and that in-cloud oxidation formation of NO_3^- may be important.

4. Implication and Application to Models

Models using a linear scavenging scheme are typically applied for deposition calculation over a period of one month to one year. Let us suppose that over this time period n_k trajectory end points arrive at a receptor during precipitation events after a travel period of $k\Delta t$ hr, where Δt is the time step of computation in the model and k is the number of time steps.

The n_k trajectory end points might encounter several precipitation events over this time period. The question is, what is the effect on model calculation of wet deposition at the receptor by using a constant versus a variable W where W is allowed to vary between the precipitation events?

To answer this question we note that the mean deposition rate of the ensemble, obtained by averaging over n_k trajectories, is given by the following:

$$\bar{D} = \left[\frac{3}{2}\bar{C}_2\bar{\Lambda}_2 + \bar{C}_4\bar{\Lambda}_4\right]h \tag{1}$$

where D is the average rate of wet SO_4^{2-} deposition, C_2 the mean SO_2 air concentration, C_4 the mean SO_4^{2-} air concentration, $\bar{\Lambda}_2$ the mean scavenging coefficient for SO_2, $\bar{\Lambda}_4$ the mean scavenging coefficient for SO_4^{2-} and h the mixed layer height.

We are concerned here only about the deposition at a fixed receptor averaged over several events. This is different from the average effects along a single trajectory.

The critical parameters in (1) are $\bar{C}_2$ and $\bar{C}_4$ which depend on how Λ_2 and Λ_4 vary between the trajectories encountering precipitation events.

$\bar{C}_2$ and $\bar{C}_4$ are given as follows:

$$\bar{C}_2 = \int_0^\infty C_2(\Lambda_2 t)\, p(\Lambda_2)\, d\Lambda_2 \tag{2}$$

and $$\overline{C}_4 = \int_0^\infty \int_0^\infty C_4(\Lambda_2 t\,;\ \Lambda_4 t)\, p(\Lambda_2, \Lambda_4)\, d\Lambda_2 d\Lambda_4 \tag{3}$$

Here C_2 and C_4 are expressed as functions of Λ_2 and Λ_4. We assume that Λ_2 and Λ_4 are determined by the same physical processes and therefore, $\Lambda_2/\Lambda_4 = \alpha$, a constant. The probability density functions $p(\Lambda_2)$ and $p(\Lambda_4)$ possess similar shapes differing only by the constant factor α.

It is general practice in modelling to approximate C_2 and C_4 by the following:

$$\overline{C}_2 = C_2\ (\overline{\Lambda}_2 t\ ) \tag{4}$$

and $$\overline{C}_4 = C_4\ (\overline{\Lambda}_2 t\ ;\ \overline{\Lambda}_4 t\ ) \tag{5}$$

To illustrate the difference between (2) and (4) as well as (3) and (5), let us consider $\overline{C}_2$. Its ratio R as calculated by (2) and (4) is given by the following:

$$R = \frac{\int_0^\infty C_2(\Lambda_2 t\ )\, p(\Lambda_2)\, d\Lambda_2}{C_2(\overline{\Lambda}_2 t\ )} \tag{6}$$

It is noted that since Λ_2 ranges from 0 to ∞ and C_2 $(\Lambda_2 t)$ is a decaying function of $\Lambda_2 t$, there is a range of values of Λ_2 for which C_2 $(\Lambda_2 t)$ decays slower than C_2 $(\overline{\Lambda}_2 t)$. Thus the ratio, $C_2(\Lambda_2 t)/C_2\ (\overline{\Lambda}_2 t)$, will be an increasing function of t in the range, $0 \leq \Lambda_2 \leq \overline{\Lambda}_2$. In other words, R will increase with t.

This implies that we will underpredict C_2 by using equation (4), as travel time increases. Similar conclusions can be reached for C_4. In areas

considerably removed from source areas we will underpredict the concentration of SO_2 by using an average value of Λ_2 in modelling rather than a variable Λ_2. Precisely where we will begin to observe this difference and its magnitude will depend on the value of $\bar{\Lambda}_2$ and the frequency with which precipitation occurs along the trajectories. This will be further investigated in a Lagrangian long range transport model.

5. Conclusions

The following conclusions are drawn from this study.

1. The scavenging ratios of S and N species are highly variable with a range spanning two orders of magnitude.
2. The scavenging ratios are log-normally distributed. The reason for this distribution is as yet unclear.
3. Using an average value of the scavenging ratio in linear long range transport models may lead to serious errors in model predictions at remote areas. The use of a variable scavenging ratio based on the distribution presented here is recommended.
4. SO_4^{2-} scavenging ratios show little spatial variability. NO_3^- scavenging ratios show greater spatial variability.
5. The larger than unity ($W_6 \times 10^{-6}$) scavenging ratios for NO_3^- suggest that in-cloud formation of NO_3^- may be important.

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Table 1

Summary of Scavenging Ratio ($W_1 = S\text{-}SO_4^{2-}$ (precip.)/$S\text{-}SO_4^{2-}$ (air)) Results

Station	N	Non Transformed Data D_{stat}	Non Transformed Data $D_{0.05}$	Log Transformed Data D_{stat}	Log Transformed Data $D_{0.05}$	$W_1 (\times 10^{-6})$ Geom. Mean	$W_1 (\times 10^{-6})$ Geom. Std. Dev.
Charleston Lake	216	0.335	0.0924	0.0526	0.0924	0.86	3.02
Dorset	330	0.385	0.0748	0.0732	0.0748	0.88	3.38
Fernberg, Mn	93	0.379	0.1408	0.0757 (N = 92)	0.1408	0.70	3.20
Longwoods	197	0.481	0.0968	0.0700	0.0968	0.82	2.86

Table 2

Summary of Scavenging Ratio ($W_2 = S\text{-}SO_4^{2-}$ (precip.)/$S\text{-}SO_2$ (air)) Results

		Non Transformed Data		Log Transformed Data		$W_2 (\times 10^{-6})$	
Station	N	D_{stat}	$D_{0.05}$	D_{stat}	$D_{0.05}$	Geom. Mean	Geom. Std. Dev.
Charleston Lake	213	0.385	0.0931	0.0417	0.0931	0.46	4.63
Dorset	284	0.413	0.0806	0.0361	0.0806	0.50	4.80
Fernberg, Mn	71	0.349	0.161	0.0704	0.161	0.76	4.70
Longwoods	189	0.336	0.0988	0.0443	0.0988	0.34	3.91

Table 3

Summary of Scavenging Ratio ($W_3 = S\text{-}SO_4^{2-}$ (precip.)/($S\text{-}SO_2$ (air) + $S\text{-}SO_4^{2-}$(air))) Results

		Non Transformed Data		Log Transformed Data		$W_3 (\times 10^{-6})$	
Station	N	D_{stat}	$D_{0.05}$	D_{stat}	$D_{0.05}$	Geom. Mean	Geom. Std. Dev.
Charleston Lake	216	0.254	0.0924	0.067	0.0924	0.26	3.36
Dorset	294	0.372	0.0792	0.0465	0.0792	0.29	3.71
Fernberg, Mn	93	0.415	0.1408	0.086 (N = 92)	0.1408	0.37	3.56
Longwoods	190	0.275	0.0985	0.0587	0.0985	0.22	3.19

Table 4

Summary of Scavenging Ratio ($W_4 = N\text{-}NO_3^-$ (precip.pt)/$N\text{-}NO_3^-$ (air)) Results

		Non Transformed Data		Log Transformed Data		W_4(x 10^{-6})	
Station	N	D_{stat}	$D_{0.05}$	D_{stat}	$D_{0.05}$	Geom. Mean	Geom. Std. Dev.
Charleston Lake	200	0.363	0.0960	0.0442 (N = 199)	0.0962	5.64	4.23
Dorset	263	0.365	0.0837	0.0450 (N = 261)	0.0841	18.63	5.71
Fernberg, Mn	45	W* = 0.600	-	W = 0.965 (N = 44)	-	7.61	5.46
Longwoods	192	0.425	0.0980	0.0843	0.0980	2.41	4.28

* The Shapiro-Wilk Statistics

Table 5

Summary of Scavenging Ratio ($W_5 = N\text{-}NO_3^-$ (precip.)/$N\text{-}HNO_3^-$ (air)) Results

Station	N	Non Transformed Data		Log Transformed Data		$W_5 (\times 10^{-6})$	
		D_{stat}	$D_{0.05}$	D_{stat}	$D_{0.05}$	Geom. Mean	Geom. Std. Dev.
Charleston Lake	212	0.246	0.0933	0.0614	0.0933	1.49	2.58
Dorset	335	0.429	0.0742	0.0751 (N = 332)	0.0745	1.82	2.98
Fernberg, Mn	92	0.382	0.142	0.0890 (N = 89)	0.144	2.51	3.40
Longwoods	193	0.302	0.098	0.0603	0.098	1.38	3.09

Table 6

Summary of Scavenging Ratio ($W_6 = N\text{-}NO_3^-$ (precip.)/($N\text{-}NO_3^-$(air) + $N\text{-}HNO_3^-$ (air))) Results

Station	N	Non Transformed Data D_{stat}	$D_{0.05}$	Log Transformed Data D_{stat}	$D_{0.05}$	W_6(x 10^{-6}) Geom. Mean	Geom. Std. Dev.
Charleston Lake	213	0.256	0.0931	0.0600	0.0931	1.06	2.55
Dorset	332	0.395	0.0745	0.0652	0.0745	1.53	2.86
Fernberg, Mn	88	0.343	0.1448	0.0822	0.1448	2.09	3.42
Longwoods	198	0.301	.0965	0.0669	.0965	0.74	2.67

KEY WORDS

SCAVENGING RATIOS
ACIDIC POLLUTANTS
MEAN SCAVENGING RATIOS
VARIABLE SCAVENGING RATIOS
LOG-NORMAL DISTRIBUTION
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